



SYNTHESIS OF NANOMATERIALS BY PHYSICAL AND CHEMICAL METHODS

Anuradha Yadav

Nanomaterials and Sensors Research Laboratory, Department of Physics, University of Lucknow, Lucknow-226007, U.P., India.

ABSTRACT

Over the past decade, nanomaterials have been the subject of enormous interest. These materials, notable for their extremely small feature size, have the potential for wide-ranging industrial, biomedical, and electronic applications. Because of recent improvement in technologies to see and manipulate these materials, the nanomaterials field has seen a huge increase in funding from private enterprises and government, and academic researchers within the field have formed many partnerships. This paper describes the various techniques for synthesis of nanomaterials. There are basically two broad areas of synthesis for nanomaterials, the Top up approach and Bottom down approach. The first one holds many physical approaches, which are now in use for the fabrication and commercial production of nano materials. The chemical process offer over other methods is good chemical homogeneity, as chemical synthesis offers mixing at molecular level.

KEY WORDS: Nanomaterials, Chemical vapour deposition, Precipitation and Immobilization methods.

1. INTRODUCTION

Nanomaterials can be metals, ceramics, polymeric, or composite materials. Although widespread interest in nanomaterials is recent, the concept was raised over 40 years ago. Physicist Richard Feynman delivered a talk in 1959 entitled "There's Plenty of Room at the Bottom", in which he commented that there were no fundamental physical reasons that materials could not be fabricated by maneuvering individual atoms. Nanomaterials have been produced and used by humans for hundreds of years - the beautiful ruby red color of some glass is due to gold nanoparticles trapped in the glass matrix. The decorative glaze known as luster, found on some medieval pottery, holds metallic spherical nanoparticles dispersed in a complex way in the glaze, which give rise to its special optical properties. The techniques used to produce these materials were considered trade secrets at the time, and are not wholly understood even now [1-2].

The variety of nanomaterials is great, and their range of properties and possible applications appear to be enormous, from extraordinarily tiny electronic devices, including miniature batteries, to biomedical uses, and as packaging films, super absorbents, components of armor, and parts of automobiles. General Motors claims to have the first vehicle to use the materials for exterior automotive applications, in running boards on its mid-size vans. Researchers are merely on the threshold of understanding and development, and that a great deal of fundamental work is still to be done. Fundamental electronic, magnetic, optical, chemical, and biological processes are also different at this level. Nano capsules and nano devices may present new possibilities for drug delivery, gene therapy, and medical diagnostics.

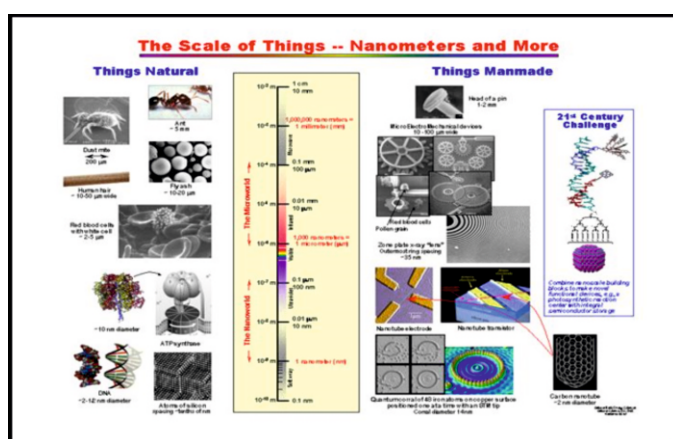


Figure 1: Naturally and Manually Build Nanomaterials.

2. SYNTHESIS OF NANOMATERIALS

Nanomaterials behave differently than other similarly-sized particles. It is therefore necessary to develop specialized approaches to synthesizing and monitoring their effects on human health and on the environment. Synthesis Methods play very important role to control the size and surface area of nanomaterials. Inert gas evaporation technique and sputtering technique are most widely used methods to produce NSMs. Apart from these, few physical as well as chemical methods are given below.

2.1 PHYSICAL METHODS

2.1.1 GAS CONDENSATION

Gas condensation was the first technique used to synthesize nanocrystalline metals and alloys. In this technique, a metallic or inorganic substantial is evaporated using thermal evaporation sources as like a Joule heated intractable containers, electron ray evaporation strategies, in an atmosphere of 1-50 m bar. Herein, a high stable gas pressure causes the creation of ultrafine elements (100 nm) by gas phase collision. Thus, very small particles are formed by impact of evaporated atoms with residual gas molecules. For this procedure, gas pressure should be greater than 3 MPa. Vaporization sources may be resistive heating, high energy electron beams, low energy electron beam and inductive heating. Clusters form near the source by homogenous nucleation in the gas phase grew by the incorporation of atoms in the gas phase. It encompasses of an ultra-high vacuum (UHV) system fit with an evaporation source, a cluster assembly device of liquid nitrogen occupied cold finger scraper assembly and compaction instrument. During heating, atoms condense in the super saturation zone close to Joule heating device [3]. The nanoparticles are removed by scraper in the form of a metallic plate. Evaporation is to be completed by using W, Ta, or Mo refractory metallic containers. If the metals react with crucibles, electron beam evaporation technique is to be used but the method is extremely slow. Sputtering or laser evaporation may be used instead of thermal evaporation. Sputtering is a non-thermal process in which surface atoms are physically ejected from the surface by momentum transfer from an energetic bombarding species of atomic/molecular size. Typical sputtering uses a glow discharge or ion beam. Interaction events which occur at and near the target surface during the sputtering process in magnetron sputtering has advantage over diode and triode sputtering. In magnetron sputtering, most of the plasma is confined to the near target region. Other alternate energy sources which have been successfully used to produce clusters or ultrafine particles are sputtering electron beam heating and plasma methods.

2.1.2 VACUUM DEPOSITION AND VAPORIZATION

In vacuum deposition process, elements, alloys, or compounds are vaporized and deposited in a vacuum. The vaporization source is the one that vaporizes materials by thermal processes. The process is carried out at pressure of less than 0.1 Pa (1 m Torr) and in vacuum levels of 10 to 0.1 MPa. The substrate temperature ranges from ambient to 500°C. The saturation or equilibrium vapor pressure of a material is defined as the vapor pressure of the material in equilibrium with the solid or liquid surface. For vacuum deposition, a reasonable deposition rate can be obtained if the vaporization rate is high. A useful deposition rate is obtained at a vapor pressure of 1.3 Pa (0.01 Torr).

Vapor phase nucleation can occur in dense vapor cloud by multibody collisions, the atoms are passed through a gas to offer necessary collision and cooling for nucleation. These particles are in the range of 1 to 100 nm and are called ultrafine particles or clusters. The advantages associated with vacuum deposition process are high deposition rates and economy. However, the deposition of many compounds is difficult. Nanoparticles produced from a supersaturated vapor are usually larger than the cluster.

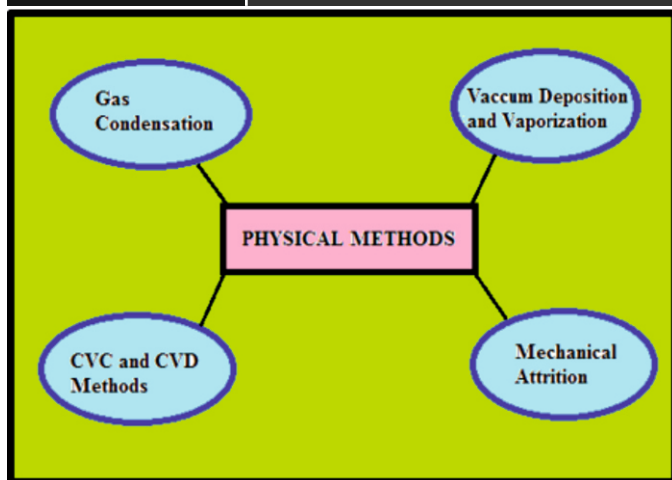


Figure 2: Physical methods for synthesis of nano materials.

2.1.3 CHEMICAL VAPOUR DEPOSITION (CVD) AND CHEMICAL VAPOUR CONDENSATION (CVC)

CVD is a well-known process in which a solid is deposited on a heated surface via a chemical reaction from the vapor or gas phase. CVC reaction needs activation energy to continue and this can be given by several methods. In thermal CVD, the reaction is activated by an elevated temperature above 900°C. A typical apparatus forms of gas supply system, deposition chamber and an exhaust system. In plasma CVD, the reaction is activated by plasma at temperatures between 300 and 700°C. In laser CVD, pyrolysis occurs when laser thermal energy heats an absorbing substrate. In photo-laser CVD, the chemical reaction is induced by ultra violet radiation which has sufficient photon energy, to break the chemical bond in the reactant molecules [4]. In this process, the reaction is photon activated and deposition occurs at room temperature. Nano composite powder has also been prepared by CVD.

2.1.4 MECHANICAL ATTRITION

Mechanical attrition produces its nanostructures not by cluster assembly but by the structural decomposition of coarser grained structures because of plastic deformation. The ball milling and rod milling techniques belong to the mechanical alloying process which has received much attention as a powerful tool for the fabrication of several advanced materials. Mechanical alloying is a unique process, which can be carried out at room temperature. The process can be performed on high energy mills, centrifugal type mill and vibratory type mill, and low energy tumbling mill. High energy mills include: Attrition Ball Mill, Planetary Ball Mill, Vibrating Ball Mill, Low Energy Tumbling Mill, and High Energy Ball Mill [5].

2.2 CHEMICAL METHODS

The advantage of chemical synthesis methods is its versatility in designing and synthesizing new materials that can be refined in to final product. There are several methods such as precipitation methods in which nano particles are found in the precipitate form while Immobilization methods give the particles in form of ash or powder.

2.2.1 PRECIPITATION METHOD

2.2.1(a) MODIFIED EMULSION PRECIPITATION METHOD

This method offers the advantage of avoiding agglomeration of the particles formed in the individual bubbles. This in turn makes possible later processing routes at unusually low temperatures [6,49-50]. To take full advantage of the method for multicomponent oxides precipitation routes need to be designed so that an intimate mixture of atoms is formed during precipitation and chemical homogeneity is kept during later processing. This offers special challenges since emulsion co-precipitations tend to be carried out with sample precursors that do not affect emulsion stability but generally show a tendency to precipitate at different rates leading to at least partial phase segregation.

This method involves the preparation of thermally stable emulsion systems prepared by adding proper amounts of surfactants to a water oil system. Within the emulsion system, there are a small number of atoms per droplet. It is necessary that exchange of reactive species take place between droplets to form a stable precipitate. From the Einstein-Smoluchowski equation, the normal rate of the particle growth is faster than the equivalent rate of exchange between droplets. Therefore, the nucleation and growth in emulsions are retarded in comparison to those in homogeneous solution, avoiding the formation of large particles. Multi surfactants are effective in forming thermally stable emulsion and controlling droplet size. Other additives play a role as steric particle stabilizer after removal of water. Before the particle dispersion by filtration or decantation of the organic phase, the emulsions were prepared by mixing the oil phase (Cyclohexane or n-heptane) with tergitol surfactants and octan-1-ol as cosurfactant. To the system stoichiometric amounts of water were added followed by vigorous mixing until a translucent emulsion was formed. The emulsion was added drop wise to alcohol

solutions of alkoxides and stirred for several hours. After removal of solvents in dispersion the residue was taken up in acetone to destroy the micelles. The solid product obtained after decantation of the organic phase was dried and transformed to nanocrystalline spinels after calcinations [6].

2.2.1 (b) HYDROTHERMAL SYNTHESIS / SOLVOTHERMAL SYNTHESIS

Hydrothermal synthesis includes the various techniques of crystallizing substances from high-temperature aqueous solutions at high vapor pressures; also termed "hydrothermal method". The term "hydrothermal" is of geologic origin. Geochemists and mineralogists have studied hydrothermal phase equilibria since the beginning of the twentieth century. The crystal growth is performed in an apparatus consisting of a steel pressure vessel called autoclave, in which a nutrient is supplied along with water. A gradient of temperature is upheld at the opposite ends of the growth chamber so that the hotter end dissolves the nutrient and the cooler end causes seeds to take more growth [7].

Possible advantages of the hydrothermal method over other types of crystal growth include the ability to create crystalline phases which are not stable at the melting point. Also, materials which have a high vapour pressure near their melting points can also be grown by the hydrothermal method. The method is also particularly suitable for the growth of large good-quality crystals while keeping good control over their composition. Disadvantages of the method include the need of expensive autoclaves, and the impossibility of observing the crystal as it grows [52].

2.2.1 (c) SOL-GEL METHOD

The sol-gel process, also known as chemical solution deposition (CSD), is a wet-chemical technique widely used in the fields of materials science and ceramic engineering. Such methods are used primarily for the fabrication of materials (typically a metal oxide) starting from a chemical solution (or sol) that acts as the precursor for an integrated network (or gel) of either discrete particles or network polymers. Typical precursors are metal alkoxides and metal chlorides, which undergo various forms of hydrolysis and polycondensation reactions [8].

In this chemical procedure, the 'sol' (or solution) gradually evolves towards the formation of a gel-like diphasic system containing both the liquid and solid phases whose morphologies range from discrete particles to continuous polymer networks. In the case of the colloid, the volume fraction of particles (or particle density) may be so low that a significant amount of fluid may need to be removed initially for the gel-like properties to be recognized. This can be accomplished in any number of ways. The simplest method is to allow time for sedimentation to occur, and then pour off the remaining liquid. Centrifugation can also be used to accelerate the process of phase separation. Removal of the remaining liquid (solvent) phase needs a drying process, which is typically accompanied by a significant amount of shrinkage and densification [9]. The rate at which the solvent can be removed is ultimately figured out by the distribution of porosity in the gel. The ultimate microstructure of the final part will clearly be strongly influenced by changes imposed upon the structural template during this phase of processing.

Afterwards, a thermal treatment, or firing process, is often necessary in order to favor further polycondensation and enhance mechanical properties and structural stability via final sintering, densification and grain growth. One of the distinct advantages of using this methodology as opposed to the more traditional processing techniques is that the densification is often achieved at a much lower temperature. The precursor sol can be either deposited on a substrate to form a film (e.g., by dip coating or spin coating), cast into a suitable container with the desired shape (e.g., to obtain monolithic ceramics, glasses, fibers, membranes, aerogels), or used to synthesize powders (e.g., microspheres, nanospheres). Sol-gel derived materials have diverse applications in optics, electronics, energy, space, sensors, medicine, reactive material and in chromatography technology.

2.2.1 (d) AEROSOL METHODS

Aerosol processes are used routinely for the commercial production of ultrafine particles ($dp < 100$ nm) and materials fabricated from them, and for pilot and laboratory scale production as well. Aerosol reaction engineering refers to the design of such processes, with the goal of relating product properties to the material properties of the aerosol precursors and the process conditions [10]. The most important process conditions are usually the aerosol volume concentration (volume of particles per unit volume of gas) and the time/temperature history of the system.

Fine particle formation by aerosol processes almost always takes place by gas-to-particle conversion. Condensable molecules produced by physical or chemical processes self-nucleate to form particles. Lots of investigations have done made to demonstrate novel methods for particle synthesis or to elucidate the mechanisms of particle formation.

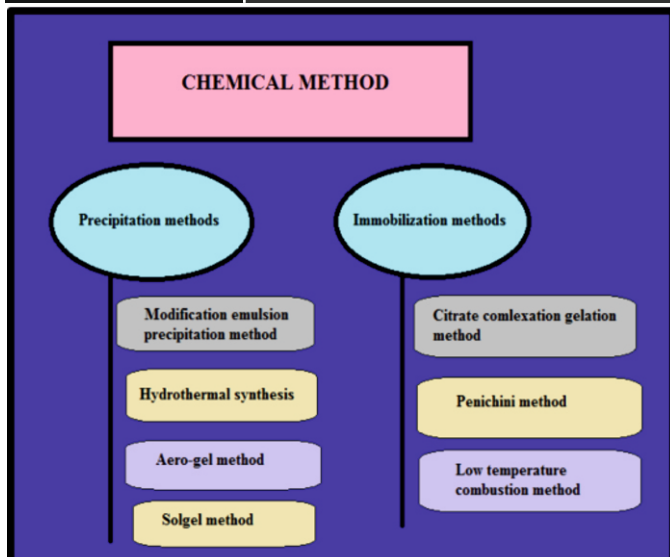


Figure 3: Chemical synthesis of Nanomaterials.

2.2.2 IMMOBILIZATION METHODS

2.2.2 (a) CITRATE-GEL METHODS

In this method, metal ions are stabilized by an organic system in precursor solutions, therefore fine oxide ashes are found afterwards a heating procedure. They have the capability of preparing multi-component compositions with good homogeneity and control of stoichiometry. These methods use poly-chelates between the C-O legends of citric acid and metal ions. The chelates undergo polyesterification on heating with a polyfunctional alcohol. In the citrate method, the chelating process occurs during the evaporation of the precursor solution having metal salts in addition to citric acid. Additional heating gives a sticky mastic, and a stiff, crystal clear, smooth gel. Mixtures of various metal ions become restrained in an early stage of the establishment of this rigid system [11]. This greatly reduces the risk of segregation into different oxide compositions during succeeding calcinations.

2.2.2 (b) PENCHINI METHOD

The process of the Penchini method is almost the same as that of the Citrate-gel method, except that metal nitrates are dissolved in alcohol, instead of water [12].

2.2.2 (c) LOW TEMPERATURE COMBUSTION SYNTHESIS METHOD

The low temperature ignition synthesis has shown to be an innovative, very simplistic, time saving and energy-efficient technique for the synthesis of ultra-fine powders. This is based on crystallizing and consequent combustion of an aqueous precursor having salts of the desired metals and some organic fuels, giving a voluminous and cottony product with large surface area. Reacting metallic salts for instance metal nitrates, and an amalgamation agent (fuel) for example citrate acid, polyacrylic mordant or urea are used as the preliminary ingredients. Citrate acid is extensively used, meanwhile it not individual functions as a reductant agent, but also a chelating mediator. The molar ratio of fuel to nitrates in the original mixture enforces an excessive impact on calcination state and the consequent features of the synthesized particles. By controlling the CA/NO₃ ratio and calcination temperature, regular crystal-like spinel powders are ready with a nanoscale prime particle size [13].

CONCLUSIONS:

Nanomaterials are not simply another step-in miniaturization, but a different arena entirely; the nanoworld lies midway between the scale of atomic and quantum phenomena, and the scale of bulk materials. It also describes the synthesis techniques of nanomaterials, by top up and bottom up approach. Sol-gel processing has been of major importance for organic-inorganic hybrids and the preparation of innovative precursors which are useful and they yield fine ceramic nanoparticles. Hydrothermal synthesis involves the same principle of hydrolysis of solution species as in the sol-gel method, but without the calcinations step needed in the latter one. Emulsion precipitation methods are convenient for single element nanoscale ceramic particles, while they are less suitable for producing multi-component ceramics.

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